1-1-2005

The stability of cementite formed from Hematite and Titanomagnetite ore under carburising atmosphere

R Longbottom
University of Wollongong, rayl@uow.edu.au

D Young
University of New South Wales

J Zhang
University of New South Wales

O Ostrovski
University of New South Wales

John Floyd International Symposium on

SUSTAINABLE DEVELOPMENTS in METALS PROCESSING

Edited by

M. Nilmani & W. J. Rankin

ISBN: 0-646-44868-4

This book is produced by NCS Associates (Australia) Pty Ltd

For additional copies contact **ncsassociates@gmail.com**

John Floyd International Symposium on
SUSTAINABLE DEVELOPMENTS IN METALS PROCESSING
July 3 - 6, 2005, Melbourne, Australia.
Edited by M. Nilmani & W. J. Rankin — nilmani@vsnl.com

The Stability of Cementite formed from Hematite and Titanomagnetite Ore Under Carburising Atmosphere

R. Longbottom, D. Young, J. Zhang and O. Ostrovski.

School of Materials Science and Engineering, UNSW,
Sydney 2052 Australia

Abstract

The decomposition of cementite formed from hematite and pre-oxidised titanomagnetite was investigated in the temperature range from 500°C to 925°C for hematite, and from 300°C to 1100°C for titanomagnetite under a carburising atmosphere in a fixed bed reactor. For hematite, cementite was most stable at temperatures 750-770°C. The decomposition rate increased with decreasing temperature between 750°C and 600°C and with increasing temperature above 770°C. For ironsand, cementite was most stable in the temperature range 700-900°C. The rate of decomposition of cementite increased with decreasing temperature between 700°C and 400°C and with increasing temperature above 900°C. Cementite formed from ironsand was more stable than cementite formed from hematite.

1 Introduction

In the reduction of iron ore, cementite is formed by the reaction of iron oxides with carburising gases, such as methane or carbon monoxide [1-11]. However, cementite is thermodynamically unstable, and decomposes to metallic iron and graphite, even under strongly carburising atmospheres [7-10]. The process of decomposition of cementite in direct reduction is akin to the metal dusting of iron-based alloys.

Zhang *et al.* [7-10] and Nakagawa *et al.* [11] have reported an unusual relationship between the stability of cementite and temperature; the rate of cementite decomposition increased with decreasing temperature in the temperature range 725-550°C.

To gain further understanding of mechanism of cementite decomposition, the authors of this paper studied the stability of cementite formed from hematite ore and titania-ferrous ore. The decomposition of cementite formed from iron ore under a carburising atmosphere, was

studied in the temperature range of 500°C to 850°C for the hematite ore, and 450°C to 900°C for the titanomagnetite ore.

2 Experimental

Cementite was formed from hematite iron ore by reaction with a CH_4-H_2-Ar gas mixture in a vertical tube furnace. The experimental set-up was described elsewhere [9]. The gas mixture of given composition was made by mixing ultra-high purity argon, methane and hydrogen whose flow rates were controlled by mass flow controllers. During this study, the gas flow rate was maintained at 1 $L \cdot min^{-1}$.

The compositions of the two iron ores used are given in **Table 1**. The hematite ore from Mt. Whaleback was used in the size range of –450 +355 mm. The size fraction used for the New Zealand ironsand was –255 +150mm. The ironsand was preoxidised by heating it within a muffle furnace in air to 1000°C for 4 days. This changed the ore from the initial titanomagnetite to a more easily reduced titanohematite.

Table 1: Composition of iron ores investigated (wt%).

Ore	Fe(tot)	SiO_2	Al_2O_3	TiO_2	P	CaO	K_2O	S	MgO
Mt. Whaleback	62.7	5.35	3.61	0.09	0.087	0.016	0.03	0.028	–
NZ ironsand	57.2	2.17	3.59	7.43	–	0.67	–	–	2.94

Cementite samples were prepared within the lab-scale fixed reactor at 750°C by passing the reducing/carburising gas, with a composition of 35 vol% CH_4, 55% H_2 and 10% Ar, through the sample for 15 minutes for the hematite ore, and 30 minutes for the ironsand. After this, the temperature of the sample was changed to the experimental temperature for cementite decomposition, and the sample held for a prescribed period, after which the sample was quenched under argon.

The phase composition of the samples was determined quantitatively by XRD using a copper Ká source. The scans were done at a rate of 1°/ min with a step size of 0.2° 2è. The morphology of the samples was examined by both optical microscopy and SEM. Etching of the optical microscopy samples in a basic sodium picrate solution allowed differentiation between cementite and metallic iron.

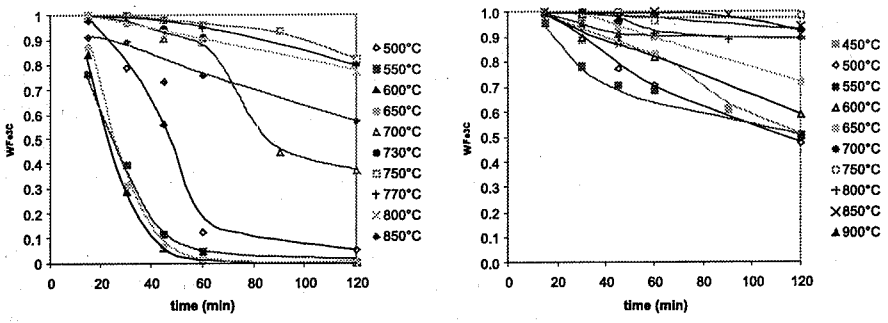
3 Results

The mass fraction of cementite formed from hematite ore during the decomposition of the cementite at different temperatures is shown in **Fig. 1(a)**. This mass fraction only takes into account the iron containing phases, neglecting gangue and free carbon. The cementite is most stable at temperatures around 750-770°C. At temperatures higher than this, the rate of cementite decomposition increased with increasing temperature. At temperatures between 730°C and 600°C, the rate of decomposition of cementite increased with decreasing temperature. Decomposition occurred most quickly at around 600-650°C.

The mass fraction of cementite formed from titania-ferrous ore (ironsand) during the decomposition of the cementite at different temperatures is shown in **Fig. 1(b)**. This cementite decomposed significantly more slowly than cementite formed from the hematite. The cementite was found to most stable between the temperatures from 700-850°C. In this range, the temperature was found to have little impact on the rate of the decomposition. At higher temperatures, the decomposition occurred slightly faster. However, the rate of decomposition of cementite increased with decreasing temperature below 700°C.

The relationship between the decomposition rate and temperature is shown in **Fig. 2**. For cementite formed from hematite a sharp increase in the decomposition rate occurs as the temperature changes from 730°C to 650°C. Above 750°C and below 650°C, the decomposition rate increases with increases in temperature. Fig. 2 shows that in the temperature range from 500°C to 850°C, cementite formed from hematite is most stable at around 750°C, and least stable at around 600°C.

The rate of decomposition of cementite formed from ironsand can be seen to increase with decreasing temperature from around 700°C to 400°C. However, the increase in the rate of decomposition is much gentler than that seen for the hematite ore between 700°C and 600°C, and indeed the rate of decomposition never increases to match that seen for cementite formed from the hematite ore.



(a) (b)

Fig. 1: Mass fractions of cementite formed from iron ore during decomposition at different temperatures.
(a) Hematite; and (b) Pre-oxidised ironsand.

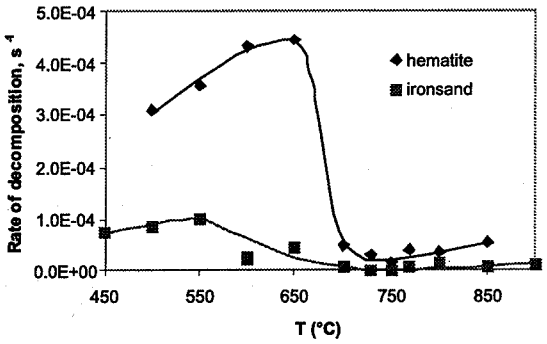


Fig. 2: The rate of decomposition of cementite as a function of temperature.

4 Discussion

The following mechanism for the decomposition of the cementite formed from iron ore under carburising atmosphere is proposed. After conversion of iron to cementite, solid carbon is deposited onto the surface of cementite. This decreases the carbon activity at the cementite/carbon interface to unity, making cementite thermodynamically unstable. Because of this, cementite is transformed to super-saturated carbon solution in metallic iron. This stage includes the nucleation and growth of the new super-saturated iron phase within the cementite. The final stage is carbon precipitation from the super-saturated solution by diffusion under gradient of carbon chemical potential. The location of the carbon could not be determined from either optical or electron microscopy. However, it is speculated that the carbon would be deposited onto the surface of the metallic iron (or existing iron-carbon interfaces), either at the outside of the particle, or inside of the pores within the particle.

The TTT curves of cementite decomposition are typical C-curves, which are explained by different rates of nucleation and growth of phases at different temperatures: slow nucleation rate at high temperatures, and slow mass transfer at low temperatures. Nucleation rate in the process of cementite decomposition is low at high temperatures because of a weak thermodynamic driving force. This driving force increases with decreasing temperature, causing the cementite decomposition rate to increase with decreasing temperature from 730°C to 550°C for hematite ore and from 700°C to 400°C for the titania-ferrous ore.

For cementite formed from both ores, the mechanism of cementite decomposition is the same, but the rate of nucleation of iron phase is different. For cementite formed from ironsand, nucleation is the rate controlling stage between 400°C and 700°C, while for cementite produced by reduction of hematite it is controlling between 550°C and 730°C.

In the process of decomposition of cementite formed from the ironsand, metallic iron precipitates in two locations as illustrated in **Fig. 3**. At high temperatures, iron preferentially precipitates around the edges of the particle (Fig. 3a). The decomposition process progresses slowly toward the particle centre. In this case, carbon activity within the particle is maintained at the high level, sufficient for existence of cementite. It drops to unity at the iron/cementite interface where the decomposition reaction takes place.

At low temperatures, iron precipitates in the particle interior (Fig. 3b). In this case, carbon activity is below the level needed for the cementite stability across the particle, and rate of nucleation and cementite decomposition is relatively fast.

(a) (b)

Fig. 3: Cross sections of cementite formed from ironsand, decomposed for (a) 60 min at 750°C; and (b) 15 min at 550°C.

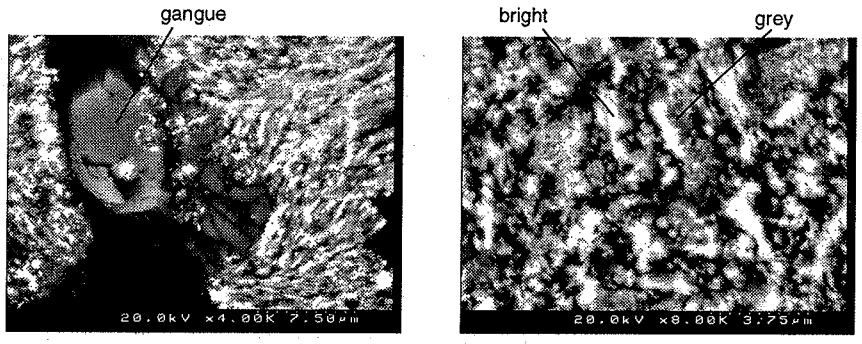
The chemistry of the two ores is significantly different. The main differences in composition are the titanium content and the amount of basic oxides.

Titanium is known as a strong carbide former. The distribution of titanium within the cementite particles was studied by SEM and EDS analyses. The following three titanium-containing phases were detected within the cementite particle as shown in **Fig. 4**.

1) The dense phase, which is the residual gangue, rich in oxides of silicon, calcium and other elements, as well as iron. It contains relatively little titanium in the form of oxide.
2) Grey phase with relatively high titanium concentration in comparison to the bulk material. This phase contains most of the titanium and becomes increasingly enriched with titanium as the decomposition of cementite progresses. This phase consists of titanium-rich iron-titanium oxides.
3) The bright phase is either cementite or metallic iron, depending on whether or not the cementite has decomposed or not. This phase contains 7-9 at% titanium, roughly the same concentration as initial ore.

Titanium within the carbide significantly alters its thermodynamic properties. This amount of titanium in the cementite is higher than expected

from the literature, where it was generally reported that titanium forms TiC preferentially to cementite [15,16]. Under the experimental conditions in this work, titanium carbide was not formed, due to the low temperatures used.



(a) (b)

Fig. 4: SEM images of cementite formed from ironsand, decomposed at 500°C for 60 minutes, indicating the three titanium containing phases. (a) gangue material at the particle edge; (b) oxide phase (grey) and metallic phase (bright) inside the particle.

Cementite formed from the ironsand at 750°C contains a high amount of titanium, which stabilises cementite. Titanium is known to have a strong affinity for carbon, reducing the activity of carbon within the cementite and the driving force for nucleation. Because of this, the decomposition occurs more slowly.

5 Conclusions

The decomposition of cementite formed from hematite was investigated in the temperature range from 500°C to 925°C under a carburising atmosphere. Cementite was most stable at temperatures around 750-770°C. Between 730°C and 550°C, the rate of decomposition of cementite increased with decreasing temperature, with the highest rate at around 600°C to 650°C. At temperatures both higher and lower than this interval, the rate of cementite decomposition increased.

Cementite formed from ironsand, was stable in the range of 700°C to 900°C, with no significant effect of temperature on the decomposition rate. At lower temperatures, between 700°C and 400°C, the rate of decomposition of cementite increased with decreasing temperature. At higher temperatures, the decomposition became faster, especially at temperatures above 1000°C. Cementite formed from ironsand decomposed much more slowly than that formed from hematite, especially at temperatures below 700°C.

The mechanism of decomposition of cementite was proposed. Firstly, carbon is deposited onto the surface of the cementite, decreasing the carbon activity in the system to unity, making cementite thermodynamically unstable. Cementite decomposition follows, including stages of nucleation and growth of a metallic iron phase and carbon diffusion to form graphite on a free surface.

The increase in the decomposition rate with decreasing temperature in the interval 500-730°C for the hematite ore and 400-700°C for ironsand was caused by a increasing in the driving force for nucleation with decreasing temperature. At other temperatures, the rate of decomposition is mix controlled by iron nucleation and carbon diffusion processes.

Titanium within the cementite formed from pre-oxidised ironsand was found in three main phases, a dense gangue phase at the edges of the particles; a titanium-iron oxide phase finely dispersed within the cementite, which was enriched with titanium; and the cementite/metallic iron itself, with the same titanium to iron ratio as the bulk material. The titanium within the $(Fe,Ti)_3C$ made the carbide more stable, causing nucleation control to be dominant over a large range of temperatures.

References

1. J. Becerra, M.T. Guerra and J.F. Negrete, "Production of Highly Metallized, High Carbon DRI Using In-Situ Reforming and Hot Product Discharge", *1999 Ironmaking Conference Proceedings*, 345-353 (1999).
2. R.H. Gronebaun and W. Pluschkell, "Investigations on the Iron Carbide Reaction", International Pre-Reduced Products Conference Proceedings, AIM, 258-267 (1996).
3. S. Hayashi and Y. Iguchi, "Iron Carbide Synthesis by Reaction of Iron Ore with H_2-CH_4 Gas Mixtures Containing Traces of Sulfur", *ISIJ International*, **37**[4] 345-349 (1997b).
4. S. Hayashi and Y. Iguchi, "Influence of several factors on synthesis of iron carbide from iron ore", *Ironmaking and Steelmaking*, **27**[2] 111-116 (2000).
5. K. Horii, Y. Iguchi, S. Hayashi and T. Moriya, "Kinetics of Iron Carbide Formation from Reduction Iron Ore in CO-H_2-H_2S Mixtures," *Tetsu-to-Hagané*, **89**[10] 1011-1017 (2003).
6. Jess and H. Depner, "Reduction and carburization of iron-ore in a fluidized bed by CO, H_2 and CH_4", *Steel Research*, **69**[3] 77-85 (1998).
7. J. Zhang, O. Ostrovski and K. Suzuki, "Effect of Temperature on Cementite Preparation in H_2-CH_4-Ar Gas Mixture", *Metallurgical Transactions B*, **31**[5] 1139-1142 (2000).
8. J. Zhang and O. Ostrovski, "Cementite Formation and Its Stability in Iron Carbide Process", 59th Ironmaking Conference Proceedings, ISS, 339-349 (2000).
9. J. Zhang and O. Ostrovski, "Cementite formation in CH_4-H_2-Ar gas mixture and cementite stability", *ISIJ International*, **41**[4] 333-339 (2001).
10. J. Zhang and O. Ostrovski, "Effect of sulphur on iron carbide formation and stability", *ISIJ International*, **41**[4] 340-344 (2001).
11. H. Nakagawa, T. Murayama and Y. Ono, "Production of Iron Carbide in CH_4-H_2 Mixtures", *Tetsu-to-Hagané*, **82**[4] 261-266 (1996).
12. E. Park and O. Ostrovski, "Reduction of Titania-Ferrous Ore by Carbon Monoxide", *ISIJ International*, **43**[9] 1316-1325 (2003).
13. E. Park and O. Ostrovski, "Effects of Preoxidation of Titania-Ferrous Ore on the Ore Structure and Reduction Behaviour", *ISIJ International*, **44**[1] 74-81 (2004a).
14. J.B. Wright, "Iron-Titanium Oxides In Some New Zealand Ironsands", *New Zealand Journal of Geology and Geophysics*, **7** 424-44 (1964).
15. M. Umemoto, Z.G. Liu, D.Y. Liu, H. Takaoka and K. Tsuchiya, "Characterisation of Alloyed Cementite Produced by Mechanical Alloying and Spark Plasma Sintering", *Materials Science Forum*, **386-388** 199-204 (2002).
16. H. Ohtani, T. Tanaka, M. Hasebe and T. Nishizawa, "Calculation of the Fe-C-Ti Ternary Phase Diagram", *CALPHAD*, **12**[3] 225-246 (1988).

* * *